Molecular Asymmetry in Sulphites from Optically Active Alcohols

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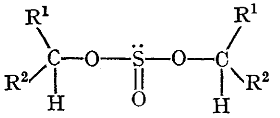
NONEQUIVALENCE of methylene protons, the subject of several recent reviews,[1] has been observed in the n.m.r. spectra of diethyl sulphite, benzyl sulphite, cyclic sulphites, and sulphoxides, and has been interpreted as being caused by conformational preferences[2] and intrinsic asymmetry[3] due to pyramidal configuration of the sulphur atom.

The sulphite of the general formula (I), prepared from natural menthol, shows nonequivalence of the proton (τ 5·66, 5·76) attached to the same carbon as the sulphite group. This novel type of molecular asymmetry would be expected in a sulphite formed from an optically active alcohol but should be absent in sulphites formed from optically inactive alcohols or in a mixed sulphite from a (+)- and a (−)-alcohol. In agreement the sulphites (I) prepared from optically active 5α-cholestan-2β-ol, -4β-ol, -4a-ol, and 5β-cholestan-3α-ol show nonequivalence of the 2α-, 4α-, 4β-, and 3β-yl protons respectively, whilst racemic secondary butanol gives a mixture of two n.m.r. distinguishable isomers formed in apparently equal proportions; one, probably formed from two molecules of (+)- or (−)-alcohol, shows nonequivalence of the methyl groups (τ 8·695, 8·70) and of the protons attached to the same carbon as the sulphite group (τ 5·37, 5·47), while the other, probably formed from one molecule of (+)- and one molecule of (−)-alcohol, shows equivalence of the methyl group (τ 8·67) and of the corresponding protons (τ 5·42). As expected, the sulphite from 4-t-butylcyclohexanol shows no asymmetry.



(I)

This type of molecular asymmetry should be exhibited by any compound with two identical asymmetric groups [both (+) or both (−)] attached to a tetrahedral atom containing two different groups or one group and a non-inverting lone pair of electrons.

No thermal isomerization of the sulphites was observed on heating to 60° but much higher temperatures (*ca.* 200°) have been necessary[4] for pyramidal inversion of sulphoxides except in the case of diallyl sulphoxide where a homolytic mechanism has been suggested.[5]

(*Received, April* 1*st*, 1968; *Com.* 398.)

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